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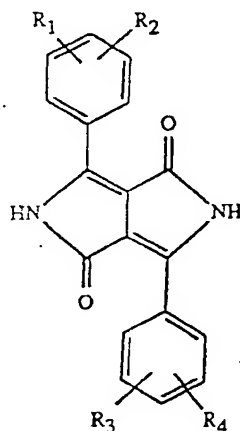
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EP 0243304 A **US 4791204 A**

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CAS ONLINE

(54) New diketopyrrolopyrrole pigment mixtures comprising both sulfonated and unsulfonated components

(57) Novel compositions comprise—

a) at least one diketopyrrolopyrrole of the formula



(I),

in which R_1 , R_2 , R_3 and R_4 are each H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or CN; and

b) 0.5 to 10 % by weight, relative to the diketopyrrolopyrrole a), of a mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles of the formula I as defined above, subject to the condition that, in at least one of these, at least one of the radicals R_1 , R_2 , R_3 and R_4 contains a group of the formula $-SO_3^-X^+$, where X^+ is H^+ or other specified cations. (Component (b) is itself novel.)

These compositions are suitable for pigmenting inks, paints and high-molecular weight organic material, and are distinguished by good rheological behaviour and by high saturation in the colourings obtained therewith.

GB 2 238 550 A

Novel compositions of matter based on diketopyrrolopyrroles

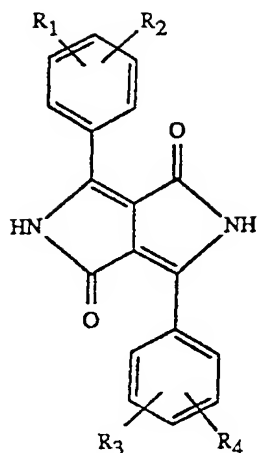
The present invention relates to novel compositions of matter containing a diketopyrrolopyrrole and a minor amount of a partially sulfonated mixture of at least 3 diketopyrrolopyrroles.

Diketopyrrolopyrroles constitute known compounds which are described, for example in US Patent Specifications 4,415,685 and 4,585,878, as pigments for colouring organic polymers. It is known from US Patent Specification 4,791,204 that it is possible to achieve improved pigment properties and also an improved rheological behaviour by admixing to a diketopyrrolopyrrole a minor amount of a diketopyrrolopyrrole which is, for example, sulfonated, carboxylated, phosphonated or N-imidomethylated. However, it has been found that the properties, even though noteworthy, of these mixtures do not always satisfy the high present-day demands of technology. In addition their preparation is laborious and accordingly expensive in terms of energy.

It has now been found that the pigment properties of diketopyrrolopyrroles, in particular their rheological behaviour and certain colouristic properties, such as, in particular, saturation, can, surprisingly, be improved to an even more considerable extent if a minor amount of an at least partially sulfonated mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles is admixed to a diketopyrrolopyrrole. In contrast with the nearest comparable sulfonated diketopyrrolopyrroles, known from US Patent Specification 4,791,204, for the preparation of which 4 stages are necessary, the sulfonated diketopyrrolopyrrole mixtures to be employed can be prepared in only two stages, consequently with considerable saving of energy and therefore with less damage to the environment.

The present application accordingly relates to a composition of matter containing

a) at least one diketopyrrolopyrrole of the formula



(I),

in which R_1 , R_2 , R_3 and R_4 independently of one another are H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or CN and

b) 0.5 to 10 % by weight, relative to the diketopyrrolopyrrole a), of a mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles of the formula I, in which R_1 , R_2 , R_3 and R_4 independently of one another are H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or a group of the formula $-SO_3^-X^+$ in which X^+ is H^+ or a group of the formulae $\frac{M^{n+}}{n}$ or $N^+(R_5)(R_6)(R_7)(R_8)$ in which M^{n+} is an n-valent metal cation, n is the numbers 1, 2 or 3, R_5 , R_6 , R_7 and R_8 independently of one another are hydrogen, C_1 - C_{18} alkyl, C_5 - C_6 cycloalkyl or phenyl which is unsubstituted or substituted by C_1 - C_{18} alkyl, or R_7 and R_8 , together with the N atom, are a pyrrolidine, imidazolidine, piperidine, piperazine or morpholine radical, or R_6 , R_7 and R_8 , together with the N atom, form a pyrrole, pyridine, picoline, pyrazine, quinoline or isoquinoline radical, subject to the condition that, in this mixture, at least one of the radicals R_1 , R_2 , R_3 or R_4 is a group of the formula $-SO_3^-X^+$.

In the compositions of matter according to the invention the diketopyrrolopyrroles of the formula I, both in component a) and in component b), are preferably diketopyrrolopyrroles in which R_2 and R_4 are hydrogen and R_1 and R_3 independently of one another are 4-Cl, 4-Br, 4- CH_3 , 4- OCH_3 , 4- C_6H_5 , 3-CN or, in particular, hydrogen and 4-Cl.

The sulfonated diketopyrrolopyrrole mixture b) is preferably admixed to the diketopyrrolopyrrole a) in amounts of 1.5 to 7 % by weight, relative to the diketopyrrolopyrrole a).

X^{\oplus} is preferably H^{\oplus} or, especially, a group of the formula $\frac{M^{n\oplus}}{n}$.

If X^{\oplus} is a group of the formula $\frac{M^{n\oplus}}{n}$, examples of $M^{n\oplus}$ are an alkali metal, alkaline earth metal, aluminium or transition metal cation, for example Na^{\oplus} , K^{\oplus} , $Mg^{2\oplus}$, $Ca^{2\oplus}$, $Sr^{2\oplus}$, $Ba^{2\oplus}$, $Mn^{2\oplus}$, $Cu^{2\oplus}$, $Ni^{2\oplus}$, $Cd^{2\oplus}$, $Co^{3\oplus}$, $Al^{3\oplus}$ and $Cr^{3\oplus}$, but particularly an alkali or alkaline earth metal cation ($n = 1$ or 2) and preferably $Ca^{2\oplus}$.

If possible substituents are C_1 - C_{18} alkyl, examples of these are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, tert-pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, heptadecyl or octadecyl.

If R_5 , R_6 , R_7 and R_8 are C_5 - C_6 cycloalkyl, examples are cyclopentyl or, particularly, cyclohexyl.

As phenyl which is substituted by C_1 - C_{18} alkyl, R_5 , R_6 , R_7 and R_8 are preferably phenyl which is substituted by C_{12} - C_{18} alkyl.

The following may be mentioned as examples of $N^{\oplus}(R_5)(R_6)(R_7)(R_8)$: $N^{\oplus}H_4$, $N^{\oplus}H_3CH_3$, $N^{\oplus}H_2(CH_3)_2$, $N^{\oplus}H_3C_2H_5$, $N^{\oplus}H_2(C_2H_5)_2$, $N^{\oplus}H_3C_3H_7$ -iso, $N^{\oplus}H_3$ -n-octadecyl, $N^{\oplus}H_3$ -cyclohexyl, $N^{\oplus}H_2$ -(cyclohexyl) $_2$, $N^{\oplus}H_2(CH_3)(C_6H_5)$, $N^{\oplus}H_3C_6H_5$, $N^{\oplus}H_3$ -p-octadecylphenyl, $N^{\oplus}(CH_3)_4$ and $N^{\oplus}(CH_3)_3$ -n-hexadecyl.

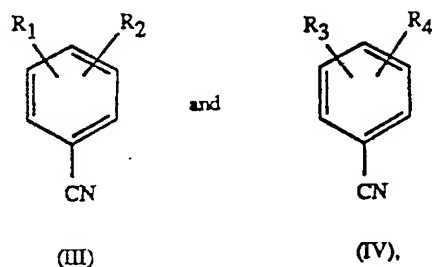
As already mentioned above, the diketopyrrolopyrroles of the formula I are known compounds.

The sulfonated diketopyrrolopyrrole mixtures b) are novel and, together with the same preferences indicated above for R_1 , R_2 , R_3 , R_4 and X^{\oplus} , are a further subject of the invention.

Their preparation, which is also a subject of this invention, is effected, for example, by reacting, in the presence of a strong base, 1 mol of a succinic acid diester of the formula



in which R is lower alkyl, with 2 mol of a mixture of two different nitriles of the formulae



in which R₁, R₂, R₃ and R₄ independently of one another are H, Cl, Br, CH₃, OCH₃ or C₆H₅, it being necessary for at least one of the radicals R₁, R₂, R₃ and R₄ to be hydrogen, in a molar ratio of III:IV of 9:1 to 1:9, preferably 3:1 to 1:3 and particularly 1:1, and subsequently sulfonating the resulting mixture by processes known per se by means of oleum, concentrated sulfuric acid, liquid sulfur trioxide or chlorosulfonic acid. The products thus obtained in two stages are then, if desired, converted into the corresponding metal or amine salt derivatives by reaction with a metal salt suitable according to the invention, for example an acetate, carbonate, chloride, nitrate or sulfate, or with an amine or amine salt.

Examples of R as lower alkyl are methyl, ethyl and particularly isopropyl, tert-butyl and tert-amyl.

The succinic acid diesters of the formula II and the nitriles of the formulae III and IV are known compounds and can be prepared by known processes.

It is appropriate to carry out the reaction of the succinic acid diester with the nitriles in an organic solvent. Examples of suitable solvents are primary, secondary or tertiary alcohols having 1 to 10 C atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 3-methyl-3-pentanol, 2-methyl-2-hexanol, 3-ethyl-3-pentanol or 2,4,4-trimethyl-2-pentanol, glycols, such as ethylene glycol or diethylene glycol, and also ethers, such as tetrahydrofuran or dioxane, or glycol ethers, such as ethylene glycol methyl ether, ethylene glycol ethyl ether, diethylene glycol monomethyl ether or diethylene glycol monoethyl ether, and also dipolar-aprotic solvents, such as acetonitrile, benzonitrile,

dimethylformamide, N,N-dimethylacetamide, nitrobenzene or N-methylpyrrolidone, aliphatic or aromatic hydrocarbons, such as benzene or benzene which is substituted by alkyl, alkoxy or halogen, such as toluene, xylene, anisole or chlorobenzene, or aromatic N-heterocyclic compounds, such as pyridine, picoline or quinoline. In addition, it is also possible to use, at the same time, the mixture of nitriles to be reacted as the solvent, if it is liquid within the temperature range in which the reaction takes place. The solvents mentioned can also be employed as mixtures. It is appropriate to use 5-20 parts by weight of solvent for 1 part by weight of reactants. An alcohol, particularly a secondary or tertiary alcohol, is preferably used as the solvent. Preferred tertiary alcohols are tert-butanol and tert-amyl alcohol.

The reaction is carried out in the presence of a strong base. Examples of suitable strong bases are alkali metal hydroxides, such as sodium, potassium or lithium hydroxide, or alkaline earth metal hydroxides, such as calcium or magnesium hydroxide, or alkali metal amides, such as lithium amide or sodium amide, or alkali metal hydrides, such as lithium hydride or sodium hydride, or alkaline earth or alkali metal alcoholates derived, in particular, from primary, secondary or tertiary aliphatic alcohols having 1 to 10 C atoms, for example sodium methylate, ethylate, n-propylate, isopropylate, n-butylate, sec-butylate, tert-butylate, 2-methyl-2-butylate, 2-methyl-2-pentylate, 3-methyl-3-pentylate or 3-ethyl-3-pentylate, potassium methylate, ethylate, n-propylate, isopropylate, n-butylate, sec-butylate, tert-butylate, 2-methyl-2-butylate, 2-methyl-2-pentylate, 3-methyl-3-pentylate or 3-ethyl-3-pentylate, or lithium methylate, ethylate, n-propylate, isopropylate, n-butylate, sec-butylate, tert-butylate, 2-methyl-2-butylate, 2-methyl-2-pentylate, 3-methyl-3-pentylate or 3-ethyl-3-pentylate, or alkaline earth or alkali metal phenates or o-alkyl-substituted phenates, such as sodium o-cresolate or potassium o-cresolate. It is also possible, however, to use a mixture of the bases mentioned.

The strong base used is preferably an alkali metal alcoholate, alkali metal being especially sodium or potassium, and the alcoholate being preferably derived from a secondary or tertiary alcohol. Examples of strong bases which are particularly preferred are therefore sodium isopropylate, sec-butylate, tert-butylate and tert-amylate or potassium isopropylate, sec-butylate, tert-butylate and tert-amylate.

The strong base can be employed in an amount of especially 0.1 to 4 mol, preferably 1.9 to 2.2 mol, relative to the reactant succinic acid diester. Depending on the reactant and the

procedure, for example in the case of recycling, smaller amounts of base can definitely have an advantageous effect on the yield. In certain cases, on the other hand, an excess of base can also exert a favourable effect on the yield. As a rule, however, stoichiometric amounts of base are sufficient.

The strong bases mentioned can be employed together with a phase transfer catalyst. This is particularly of advantage when the solubility of a specific base in a specific solvent is low. The phase transfer catalysts can be employed in an amount of 0.001 to 50 mol %, preferably 0.01 to 0.3 mol %, relative to the reactant succinic acid diester. Phase transfer catalysts which are suitable for this purpose are the customary phase transfer catalysts described in the literature, such as are listed, for example, in CHEMTECH, February 1980, page 111, Table 1, that is to say, for example, quaternary salts, cyclic polyethers, open-chain polyethers, N-alkylphosphoramides or oxides of phosphorus or sulfur having a methylene bridge.

It is appropriate to carry out the reaction at a temperature of 60 to 140°C, preferably 80 to 120°C.

In order to react the succinic acid diester with the nitriles, it is, in principle, possible initially to take all the components at a fairly low temperature and then to heat the mixture to the reaction temperature range, or to add the individual components to one another in any desired sequence within the reaction temperature range.

A preferred embodiment, which, as a rule, has a particularly favourable effect on the yield, consists in initially taking the nitrile mixture together with the base, and metering in the succinic acid diester within the reaction temperature range.

Particularly in the case of alcoholates derived from lower alcohols, for example methanol, ethanol, n-propanol, isopropanol or tert-butanol, it can prove necessary to remove the lower alcohol formed in the course of the reaction continuously from the reaction medium, in order to achieve higher yields.

If an alcohol is used as the solvent and an alcoholate as the base, it can be advantageous to select an alcohol and an alcoholate having identical alkyl moieties. Equally, it can be advantageous if, in addition, the succinic acid diester also contains just such alkyl groups.

In order to hydrolyse the condensation product it is possible to use an acid or an alcohol having 1 to 4 C atoms, such as methanol or ethanol, but preferably water. Examples of suitable acids are aliphatic or aromatic carboxylic or sulfonic acids, for example formic acid, acetic acid, propionic acid, oxalic acid, benzoic acid or benzenesulfonic acid. Suitable acids are also mineral acids, such as hydrogen chloride, an aqueous solution thereof, and carbonic acid or dilute sulfuric and phosphoric acid.

The diketopyrrolopyrrole mixture precipitates in the course of the hydrolysis and can be isolated by filtration.

In the sulfonation, the concentration to be employed of the sulfonating agent and the reaction conditions to be selected are closely connected with the number of sulfonic acid groups which are to be introduced into the diketopyrrolopyrrole mixture.

The compositions of matter according to the invention are obtained by mixing the individual components a) and b) in the desired ratio either directly in the pasting medium or in an additional mixing process in water or sulfuric acid. A double decomposition to give the desired metal salt can, if desired, also be carried out subsequently by treating the composition of matter according to the invention (containing, for example, the sodium salt) with an appropriate metal salt [for example $\text{Ca}(\text{SO}_4)$].

The compositions of matter according to the invention can be used as pigments for colouring high-molecular weight organic material.

Examples of high-molecular weight organic materials which can be coloured or pigmented with the compositions of matter according to the invention are cellulose ethers and esters, such as ethylcellulose, nitrocellulose, cellulose acetate or cellulose butyrate, natural resins or synthetic resins, such as polymerization resins or condensation resins, such as aminoplasts, particularly urea/formaldehyde and melamine/formaldehyde resins, alkyd resins, phenoplasts, polycarbonates, polyolefins, polystyrene, polyvinyl chloride, polyamides, polyurethanes, polyesters, fluorine polymers, for example polyfluoroethylene, polytrifluorochloroethylene or tetrafluoroethylene/hexafluoropropylene copolymer, and also rubber, casein, silicone and silicone resins, individually or as mixtures.

The high-molecular weight organic compounds mentioned can be present individually or as mixtures in the form of plastic compositions or melts or in the form of spinning

solutions, lacquers, paints or printing inks. Depending on the end use, it proves advantageous to employ the compositions of matter according to the invention as toners or in the form of preparations. The compositions of matter according to the invention can be employed in an amount of 0.01 to 30 % by weight, preferably 0.1 to 10 % by weight, relative to the high-molecular weight organic material to be pigmented.

The pigmentation of the high-molecular organic substances with the compositions of matter according to the invention is carried out, for example, by mixing a composition of matter of this type, if appropriate in the form of masterbatches, into these substrates using roll mills, mixing apparatus or grinding apparatus. The pigmented material is then brought into the desired final form by processes known per se, such as calendering, compression-moulding, extrusion, spread-coating, casting or injection moulding. It is often desirable to incorporate plasticizers into the high-molecular weight compounds before shaping in order to produce non-rigid shaped articles or to decrease their brittleness. Esters of phosphoric acid, phthalic acid or sebacic acid can, for example, be used as these. The plasticizers can be incorporated into the polymers before or after the incorporation of the composition of matter according to the invention. In order to achieve different colour shades, it is also possible to add, as well as the compositions of matter according to the invention, fillers or other colouring constituents, such as white, coloured or black pigments, in any desired amounts to the high-molecular weight, organic materials.

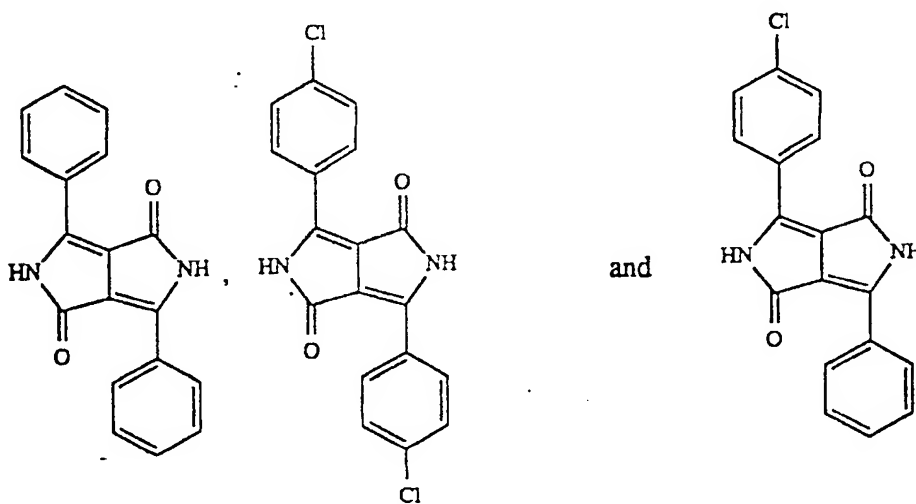
For pigmenting paints and printing inks, the high-molecular weight organic materials and the compositions of matter according to the invention are made into a fine dispersion or solution, if desired together with additives, such as fillers, other pigments, siccatives or plasticizers, in a joint organic solvent or solvent mixture. The procedure followed can be to disperse or dissolve the individual components on their own or several together and only then to combine all the components.

The colourations, for example in plastics, fibres, paints or prints, obtained with the compositions of matter according to the invention, which are characterized by good rheological properties, are distinguished by good overall properties, such as good dispersibility, high colour strength, good fastness to overlacquering, migration, heat, light and weathering, and by good gloss.

The sulfonated diketopyrrolopyrrole mixture used as the component b) in the composition

of matter according to the invention can, however, also be employed itself as a pigment for colouring the high-molecular weight organic materials listed above. It can be employed for this purpose as a crude product or after appropriate conditioning/after-treatment, for example as already described for the compositions of matter according to the invention. The following examples illustrate the invention.

Example 1 a) 120 ml of t-amyl alcohol (anhydrous) are initially placed in a sulfonation flask under nitrogen. 6.9 g of sodium and 0.1 g of the sodium salt of bis-2-ethylhexyl sulfosuccinate are added with slow stirring, and the mixture is heated to 95-102°C. The molten sodium is then kept under nitrogen overnight at 95°C, with vigorous stirring. The resulting solution is then cooled to 85°C, and a mixture of 14.04 g of 4-chlorobenzonitrile and 10.3 g of benzonitrile is added. 20.3 g of diisopropyl succinate are then metered in in the course of 2 hours at 95°C. The reaction mixture is left for 5 hours at 95°C to complete the reaction and is then cooled to room temperature. The resulting mixture is poured onto 300 ml of cold water, and the mixture is heated under reflux for 1 hour and is then subjected to steam distillation. The resulting mixture is filtered at 60°C, and the product is washed with 1000 ml of water and dried at 80°C in a vacuum oven. Yield: 23.6 g of a red powder containing essentially the compounds of the formulae



Analysis (%): found: C = 64.93; H = 3.45; N = 8.38; Cl = 13.72.

b) 160 g of 25 % oleum and 160 g of sulfuric acid monohydrate are initially placed in a sulfonation flask. 20 g of the mixture obtained in Example 1a) are introduced at 2-5°C in

the course of 30 minutes. The mixture is stirred for 20 hours at room temperature and the resulting solution is then poured onto 1000 g of ice and 280 ml of water. The resulting suspension is stirred for 15 minutes and heated to 75°C and 120 g of NaCl are then added. The mixture is stirred for one hour at 75°C to complete the reaction. The suspension is then filtered at room temperature and the material on the filter is washed with 5 % NaCl solution until the filtrate is colourless, and the material on the filter is dried in a vacuum drying cabinet. 29.0 g of a red-violet powder are obtained.

Analysis (%): C = 40.7; H = 2.3; N = 5.1; S = 4.8; Cl = 17.9.

Cl_{ion} = 9.6; H₂O = 2.4.

c) 964 g of moist (36.3 % solids content) 1,4-diketo-3,6-di-(4-chlorophenyl)-pyrrolo-[3,4-c]-pyrrole are initially placed in a sulfonation flask. The volume is made up to 8 l with demineralized water. After stirring at room temperature for one hour, a solution in 900 ml of water (60°C) of 8.1 g of the product prepared in Example 1b) is added, and the mixture is stirred at room temperature for two hours. 100 g of CaCl₂, dissolved in about 500 ml of water, are then added, and the mixture is heated to 75°C, stirred for one hour at 75°C and filtered at room temperature. The material on the filter is washed thoroughly with water and dried at 80°C in a vacuum drying cabinet. This gives 352 g of red powder having excellent colouristic and rheological properties.

Example 2-6: The procedure is as described in Example 1c), but the pigments listed in the table below are used, as moist filter cakes, instead of 1,4-diketo-3,6-di-(4-chlorophenyl)-pyrrolo-[3,4-c]-pyrrole. Pigment powders having excellent rheological and colouristic properties are obtained.

Example

- | | |
|---|-------------------------------------------------------------|
| 2 | 1,4-Diketo-3,6-di-(4-bromophenyl)-pyrrolo-[3,4-c]-pyrrole |
| 3 | 1,4-Diketo-3,6-di-(4-methylphenyl)-pyrrolo-[3,4-c]-pyrrole |
| 4 | 1,4-Diketo-3,6-di-(3-methoxyphenyl)-pyrrolo-[3,4-c]-pyrrole |
| 5 | 1,4-Diketo-3,6-di-(4-phenylphenyl)-pyrrolo-[3,4-c]-pyrrole |
| 6 | 1,4-Diketo-3,6-di-(3-cyanophenyl)-pyrrolo-[3,4-c]-pyrrole |

Example 7: The procedure is as described in Example 1c), but trimethylhexadecylammonium bromide is used instead of CaCl₂. A red pigment having excellent rheological and colouristic properties is obtained.

Example 8: The procedure is as described in Example 5, but trimethylhexadecylammonium bromide is used instead of CaCl_2 . A red pigment having excellent rheological and colouristic properties is obtained.

Example 9: The procedure is as described in Example 6, but trimethylhexadecylammonium bromide is used instead of CaCl_2 . An orange pigment having excellent rheological and colouristic properties is obtained.

Example 10: The procedure is as described in Example 1a), but a corresponding amount of 4-phenylbenzonitrile is used instead of 4-chlorobenzonitrile. The resulting red pigment powder is processed further analogously to Examples 1b) and 1c). A red pigment having excellent rheological and colouristic properties is obtained.

Example 11: The procedure is as described in Example 1a), but a corresponding amount of 4-methylbenzonitrile is used instead of 4-chlorobenzonitrile. The resulting red pigment powder is processed further analogously to Examples 1b) and 1c). A red pigment having excellent rheological and colouristic properties is obtained.

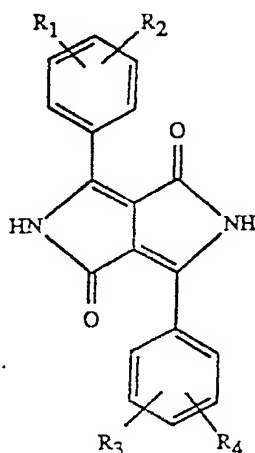
Example 12: Use in an alkyd/melamine stoving paint.

A mixture of 460 g of steatite balls of diameter 8 mm, an alkyd lacquer consisting of 58.7 g of alkyd resin, 60 % solution of [®]Alkydal F 310 (BAYER AG) in xylene, 58.7 g of alkyd resin, 60 % solution of [®]Alkydal F 32 (BAYER AG) in xylene, 2.0 g of [®]Silikonöl A, 1 % solution in xylene (BAYER AG), 4.0 g of n-butanol, 4.0 g of Dowanol, 15 g of xylene, 5.6 g of dispersing agent [®]Disperbyk D-160 (BYK-Chemie) and also 28.0 g of the pigment mixture prepared in accordance with Example 1 are dispersed for 72 hours in a glass bottle having a twist-off closure on a roller stand. After 24.0 g of the melamine component, 90 % solution of [®]Cymel 327 (Cyanamid) in xylene, have been added, the mixture is dispersed for a further hour on the roller stand. The steatite balls are then removed. The pigmented lacquer paste thus obtained is applied to [®]Milar transparent films and is then stoved for 30 minutes at 130°C (paint film thickness 50 µm). A red colouration having excellent colouristic and rheological properties is obtained.

What is claimed is:

1. A composition of matter containing

a) at least one diketopyrrolopyrrole of the formula



(I),

in which R_1 , R_2 , R_3 and R_4 independently of one another are H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or CN and

b) 0.5 to 10 % by weight, relative to the diketopyrrolopyrrole a), of a mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles of the formula I, in which R_1 , R_2 , R_3 and R_4 independently of one another are H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or a group of the formula $-SO_3^- X^+$ in which X^+ is H^+ or a group of the formulae $\frac{M^{n+}}{n}$ or $N^+(R_5)(R_6)(R_7)(R_8)$ in which M^{n+} is an n-valent metal cation, n is the numbers 1, 2 or 3, R_5 , R_6 , R_7 and R_8 independently of one another are hydrogen, C_1 - C_{18} alkyl, C_5 - C_6 cycloalkyl or phenyl which is unsubstituted or substituted by C_1 - C_{18} alkyl, or R_7 and R_8 , together with the N atom, are a pyrrolidine, imidazolidine, piperidine, piperazine or morpholine radical, or R_6 , R_7 and R_8 , together with the N atom, form a pyrrole, pyridine, picoline, pyrazine, quinoline or isoquinoline radical, subject to the condition that, in this mixture, at least one of the radicals R_1 , R_2 , R_3 or R_4 is a group of the formula $-SO_3^- X^+$.

2. A composition of matter according to claim 1, wherein the diketopyrrolopyrroles of the formula I, both in a) and in b), are diketopyrrolopyrroles in which R_2 and R_4 are hydrogen

and R_1 and R_3 independently of one another are hydrogen, 4-Cl, 4-Br, 4-CH₃, 4-OCH₃, 4-C₆H₅ or 3-CN.

3. A composition of matter according to claim 1, wherein the diketopyrrolopyrroles of the formula I, both in a) and in b) are diketopyrrolopyrroles in which R_2 and R_4 are hydrogen and R_1 and R_3 independently of one another are hydrogen or 4-Cl.

4. A composition of matter according to claim 1, 2 or 3 wherein the sulfonated diketopyrrolopyrrole mixture b) is admixed to the diketopyrrolopyrrole a) in amounts of 1.5 to 7 % by weight, relative to the diketopyrrolopyrrole a).

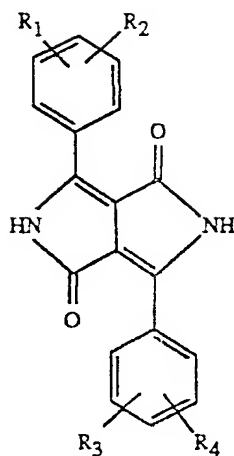
5. A composition according to any of claims 1 to 4, wherein X^{\oplus} is H^{\oplus} or a group of the formula $\frac{M^{n\oplus}}{n}$ in which $M^{n\oplus}$ is an alkali metal, alkaline earth metal, aluminium or transition metal cation.

6. A composition of matter according to claim 5, wherein X^{\oplus} is a group of the formula $\frac{M^{n\oplus}}{n}$ in which $M^{n\oplus}$ is an alkali metal or alkaline earth metal cation and n is the numbers 1 or 2.

7. A composition of matter according to claim 1, wherein X^{\oplus} is a calcium cation.

8. A composition according to claim 1, substantially as described in any of Examples 1 to 11.

9. A mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles of the formula 1



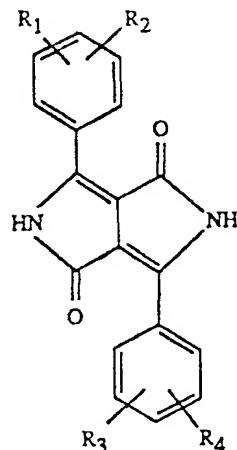
(I),

in which R_1 , R_2 , R_3 and R_4 independently of one another are H, Cl, Br, CH_3 , OCH_3 , C_6H_5 or a group of the formula $-SO_3^{\ominus}X^{\oplus}$ in which X^{\oplus} is H^{\oplus} or a group of the formulae

$\frac{M^{n\oplus}}{n}$ or $N^{\oplus}(R_5)(R_6)(R_7)(R_8)$ in which $M^{n\oplus}$ is an n-valent metal cation, n is the

numbers 1, 2 or 3, R_5 , R_6 , R_7 and R_8 independently of one another are hydrogen, C_1 - C_{18} alkyl, C_5 - C_6 cycloalkyl or phenyl which is unsubstituted or substituted by C_1 - C_{18} alkyl, or R_7 and R_8 , together with the N atom, are a pyrrolidine, imidazolidine, piperidine, piperazine or morpholine radical, or R_6 , R_7 and R_8 , together with the N atom, form a pyrrole, pyridine, picoline, pyrazine, quinoline or isoquinoline radical, subject to the condition that, in this mixture, at least one of the radicals R_1 , R_2 , R_3 or R_4 is a group of the formula $-SO_3^{\ominus}X^{\oplus}$.

10. A process for the preparation of a mixture of at least 3 different symmetrical and unsymmetrical diketopyrrolopyrroles of the formula I

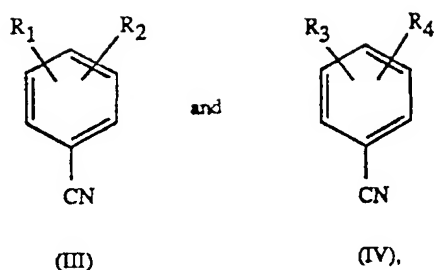


(I),

in which R₁, R₂, R₃ and R₄ independently of one another are H, Cl, Br, CH₃, OCH₃, C₆H₅ or a group of the formula -SO₃[⊖]X[⊕] in which X[⊕] is H[⊕] or a group of the formulae $\frac{M^{n\oplus}}{n}$ or N[⊕](R₅) (R₆) (R₇) (R₈) in which M^{n⊕} is an n-valent metal cation, n is the numbers 1, 2 or 3, R₅, R₆, R₇ and R₈ independently of one another are hydrogen, C₁-C₁₈alkyl, C₅-C₆cycloalkyl or phenyl which is unsubstituted or substituted by C₁-C₁₈alkyl, or R₇ and R₈, together with the N atom, are a pyrrolidine, imidazolidine, piperidine, piperazine or morpholine radical, or R₆, R₇ and R₈, together with the N atom, form a pyrrole, pyridine, picoline, pyrazine, quinoline or isoquinoline radical, subject to the condition that, in this mixture, at least one of the radicals R₁, R₂, R₃ or R₄ is a group of the formula -SO₃[⊖]X[⊕], by reacting 1 mol of a succinic acid diester of the formula



in which R is lower alkyl, in the presence of a strong base, with 2 mol of a mixture of two different nitriles of the formulae



in which R₁, R₂, R₃ and R₄ independently of one another are H, Cl, Br, CH₃, OCH₃ or C₆H₅, it being necessary for at least one of the radicals R₁, R₂, R₃ and R₄ to be hydrogen, in a molar ratio of III:IV of 9:1 to 1:9, and subsequently sulfonating the resulting mixture by processes known per se by means of oleum, concentrated sulfuric acid, liquid sulfur trioxide or chlorosulfonic acid.

11. A high-molecular weight organic material containing a composition of matter according to any of claims 1 to 8.

12. A high-molecular weight organic material containing a mixture according to claim 9.